

Open Research Online

The Open University's repository of research publications
and other research outputs

On the electron-induced isotope fractionation in low temperature $^{32}\text{O}_2/^{36}\text{O}_2$ ices—ozone as a case study

Journal Item

How to cite:

Sivaraman, B; Mebel, A. M.; Mason, N. J.; Babikov, D. and Kaiser, Ralf (2011). On the electron-induced isotope fractionation in low temperature $^{32}\text{O}_2/^{36}\text{O}_2$ ices—ozone as a case study. *Physical Chemistry Chemical Physics*, 13(2) pp. 421–427.

For guidance on citations see [FAQs](#).

© 2011 the Owner Societies

Version: Version of Record

Link(s) to article on publisher's website:
<http://dx.doi.org/doi:10.1039/C0CP00448K>

Copyright and Moral Rights for the articles on this site are retained by the individual authors and/or other copyright owners. For more information on Open Research Online's data [policy](#) on reuse of materials please consult the policies page.

oro.open.ac.uk

On the electron-induced isotope fractionation in low temperature $^{32}\text{O}_2/^{36}\text{O}_2$ ices—ozone as a case study

B. Sivaraman,^a A. M. Mebel,^b N. J. Mason,^{*a} D. Babikov^c and R. I. Kaiser^{*de}

Received 4th May 2010, Accepted 26th October 2010

DOI: 10.1039/c0cp00448k

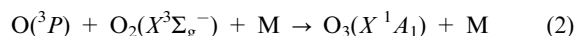
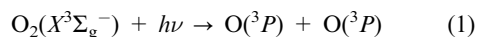
The formation of six ozone isotopomers and isotopologues, $^{16}\text{O}^{16}\text{O}^{16}\text{O}$, $^{18}\text{O}^{18}\text{O}^{18}\text{O}$, $^{16}\text{O}^{16}\text{O}^{18}\text{O}$, $^{18}\text{O}^{18}\text{O}^{16}\text{O}$, $^{16}\text{O}^{18}\text{O}^{16}\text{O}$, and $^{18}\text{O}^{16}\text{O}^{18}\text{O}$, has been studied in electron-irradiated solid oxygen $^{16}\text{O}_2$ and $^{18}\text{O}_2$ (1 : 1) ices at 11 K. Significant isotope effects were found to exist which involved enrichment of ^{18}O -bearing ozone molecules. The heavy $^{18}\text{O}^{18}\text{O}^{18}\text{O}$ species is formed with a factor of about six higher than the corresponding $^{16}\text{O}^{16}\text{O}^{16}\text{O}$ isotopologue. Likewise, the heavy $^{18}\text{O}^{18}\text{O}^{16}\text{O}$ species is formed with abundances of a factor of three higher than the lighter $^{16}\text{O}^{16}\text{O}^{18}\text{O}$ counterpart. No isotope effect was observed in the production of $^{16}\text{O}^{18}\text{O}^{16}\text{O}$ versus $^{18}\text{O}^{16}\text{O}^{18}\text{O}$. Such studies on the formation of distinct ozone isotopomers and isotopologues involving non-thermal, non-equilibrium chemistry by irradiation of oxygen ices with high energy electrons, as present in the magnetosphere of the giant planets Jupiter and Saturn, may suggest that similar mechanisms may contribute to the ^{18}O enrichment on the icy satellites of Jupiter and Saturn such as Ganymede, Rhea, and Dione. In such a Solar System environment, energetic particles from the magnetospheres of the giant planets may induce non-equilibrium reactions of suprathermal and/or electronically excited atoms under conditions, which are quite distinct from isotopic enrichments found in classical, thermal gas phase reactions.

1. Introduction

The origin of the oxygen isotopic fractionation (^{18}O vs. ^{16}O) in molecules in our Solar System such as ozone (O_3), water (H_2O), carbon monoxide (CO), and carbon dioxide (CO_2) has been a topic of experimental and theoretical studies since it was discovered nearly 30 years ago.¹ First measured in chondritic meteorites, such isotopic enrichments have been found in Martian rocks and are now routinely utilized to identify Martian meteoritic material that are deposited on Earth.^{1,2} In 1965, Taylor suggested a classification of rocks in the solar system according to their $^{18}\text{O}/^{16}\text{O}$ ratio.³ Recently Ozima *et al.*⁴ classified 400 bulk meteorite samples using their oxygen isotopic data and commented upon the similarity between solar and planetary oxygen. NASA's 'Genesis' and 'Stardust' missions measured oxygen isotopes in the solar wind

and from comet Wild 2 by collecting (and returning) 'dust' samples to the Earth.^{5,6} Such studies have provided vital information on the chemical origins of our Solar System and may reveal how the different planets were formed.⁶ Oxygen isotopes may also be used to understand the formation of the Earth–Moon system.⁷ Also, the study of oxygen isotopic variations is not confined to the Solar System; current space-based telescopes are capable of developing maps of isotopic variations in star forming regions; for example the Odin satellite has recently revealed the presence of molecular oxygen in the interstellar medium.⁸ This can be also extended to determine $^{18}\text{O}/^{16}\text{O}$ ratios in abundant, oxygen-bearing molecules such as carbon monoxide and—if detected—potentially ozone.

The ^{18}O enrichment in ozone has received particular attention. In the Earth's atmosphere, ozone is formed by the Chapman mechanism (eqn (1) and (2)), where M is a third body (usually nitrogen in the terrestrial atmosphere) necessary to stabilize the ozone molecule, which would otherwise decompose back to the reactants due to the internal energy it has upon formation. This process has been studied extensively.^{9–13} Each of the three stable oxygen isotopes ($^{18}\text{O}/^{17}\text{O}/^{16}\text{O}$) may take part in the Chapman reactions producing a wide range of isotopomers and isotopologues all of which have been measured in the terrestrial stratosphere.^{14,15} Within the terrestrial atmosphere the ratio of oxygen isotopes have been measured to be $^{18}\text{O}/^{17}\text{O} = 5.5$, $^{16}\text{O}/^{18}\text{O} = 500$, $^{16}\text{O}/^{17}\text{O} = 2750$.¹⁶ Kinetic isotope effects and symmetry induced isotopic fractionation then suggest different rate constants for eqn (1) and (2) depending on the isotopes involved^{17–20} leading to distinct formation probabilities for each of the isotopomers and isotopologues. Initially, these molecules were thought to form *via* a cyclic ozone intermediate, whose ring opened to the acyclic form. However, this interpretation has been challenged, and fast isotopic exchange reactions involving ^{18}O enriched molecular oxygen ($^{16}\text{O}^{18}\text{O}$) have to be considered as well.^{21,22}



Isotopic enrichment processes may also occur within oxygen-rich ices in the Solar System.²³ However, the underlying mechanisms and reaction conditions can differ dramatically. In classical experiments,^{9–13} isotope enrichment processes were studied in the gas phase under thermal conditions where the thermal reactants have a well-defined Maxwell–Boltzmann distribution. However, high energy electrons induce a non-equilibrium chemistry in which multiple effects occur such as

^a Department of Physics and Astronomy, The Open University, Milton Keynes, MK7 6AA, UK. E-mail: n.j.mason@open.ac.uk

^b Department of Chemistry and Biochemistry, Florida International University, Miami, FL 33199, USA

^c Marquette University, Department of Chemistry, Milwaukee, WI 53201, USA

^d Department of Chemistry, University of Hawaii at Manoa, Honolulu, Hawaii 96822, USA. E-mail: rafk@hawaii.edu

^e NASA Astrobiology Institute, University of Hawaii at Manoa, Honolulu, HI 96822, USA

the generation of secondary electrons, the formation of electronically excited atoms and the generation of ground state oxygen atoms with excess kinetic energy. It must also be noted that these solid/ice experiments are not conducted under 'single collision' conditions as encountered in crossed beam experiments. Therefore, it is often difficult to untangle to what extend the products originate from, for instance, reactions of thermalized atoms or suprathermal atoms, where the latter can overcome reaction barriers easily.

Solid ozone has been detected on the frozen surfaces of Jupiter's moon Ganymede and on Saturn's satellites Rhea and Dione.^{24,25} The formation of ozone on these surfaces has then been attributed to bombardment by ions and energetic electrons from planetary magnetospheres.²⁶ However, to date, it has not been possible to determine the possible role of any isotopic fractionation of ozone in such low temperature ices. Therefore, we have investigated ^{16}O and ^{18}O isotopic enrichment processes in ozone formation in low temperature oxygen ices ($^{16}\text{O}_2$ and $^{18}\text{O}_2$) irradiated by energetic electrons. These experiments provide a simulation of the interaction of magnetospheric electrons with oxygen-bearing ices (oxygen) and may elucidate the underlying mechanisms forming ozone isotopomers and isotopologues in low temperature, oxygen-rich Solar System ices.

2. Experimental

The experiments were performed within an ultra high vacuum (UHV) chamber operating at base pressures of about 5×10^{-11} Torr.²⁷ Briefly, the ice samples were prepared on a polished silver target attached to a two stage closed loop helium cryostat capable of cooling the target down to 11 K. A mixture of $^{16}\text{O}_2$ (Gaspro; 99.99%) and $^{18}\text{O}_2$ (98% ^{18}O) was prepared in a gas mixing chamber with a ratio of 1.0: (1.0 \pm 0.01) and deposited onto the cooled target for 300 s at a chamber pressure of 10^{-7} Torr. Subliming the freshly deposited mixtures and correcting for the isotope-dependent electron impact ionization cross section, a mass spectrometric quantification of the subliming molecules at $m/z = 32$ ($^{16}\text{O}_2^+$) and $m/z = 36$ ($^{18}\text{O}_2^+$) suggests that there is no isotopic fractionation when condensing the gases onto the target at 11 K; therefore, within the error limits of our mass spectrometer, the $^{16}\text{O}_2$ to $^{18}\text{O}_2$ ratio in the ices is 1.00 ± 0.01 . After deposition, the ices were irradiated with 5 keV electrons for one hour. The electron beam, generated using a commercially available electron gun, was operated at 100 nA current and scanned over 1.8 ± 0.3 cm² of the target; accounting for the extraction efficiency of 78%, this exposes the target to 1.75×10^{15} electrons during the irradiation period. After irradiation the sample was left isothermally at 11 K to monitor possible reactions of trapped oxygen atoms at 11 K. Thereafter, the ices were warmed at a rate of 0.5 K min⁻¹ to 293 K. Radiation-induced chemical changes in the ice films were monitored on line and *in situ* using a Fourier transform infrared (FTIR) spectrometer operating in reflection-absorption-reflection mode with a reflection angle of 75° from the normal relative to the mirror surfaces. FTIR spectra were collected over the range of 6000–500 cm⁻¹ with an integration time of 2.5 min and at 2 cm⁻¹ resolution.

Gas phase products subliming during the warm up of the sample were monitored with a quadrupole mass spectrometer (1–200 amu).

3. Results

3.1. Infrared spectra

In the gas phase, the C_{2v} symmetric ozone molecule has three fundamental vibrational modes: the ν_1 bending mode at 701 cm⁻¹ (lowest intensity), the ν_2 symmetric stretching vibration at 1103 cm⁻¹ of medium intensity, and the most intense ν_3 asymmetric stretching mode at 1042 cm⁻¹.²⁷ In the irradiated ices, ozone was monitored *via* its most intense ν_3 fundamental around 1000 cm⁻¹. The broad spectral band lying between 960 cm⁻¹ to 1050 cm⁻¹ was deconvoluted into six distinct peaks corresponding to the six possible ozone isotopomers and isotopologues.^{28–30} Bands at 978 cm⁻¹, 988 cm⁻¹, 1002 cm⁻¹, 1012 cm⁻¹, 1022 cm⁻¹, and 1035 cm⁻¹ were assigned to $^{18}\text{O}^{18}\text{O}^{18}\text{O}$, $^{18}\text{O}^{18}\text{O}^{16}\text{O}$, $^{16}\text{O}^{18}\text{O}^{16}\text{O}$, $^{18}\text{O}^{16}\text{O}^{18}\text{O}$, $^{16}\text{O}^{16}\text{O}^{18}\text{O}$ and $^{16}\text{O}^{16}\text{O}^{16}\text{O}$, respectively (Fig. 1a). These data are in excellent agreement with literature values.^{28–30}

A weak ν_2 band was also observed in the irradiated ices (Fig. 1b). However, only the $^{18}\text{O}^{18}\text{O}^{18}\text{O}$ and $^{18}\text{O}^{18}\text{O}^{16}\text{O}$ isotopologues could be observed at 662 cm⁻¹ and 677 cm⁻¹, respectively.^{28,30,31} Two bands, at 688 cm⁻¹ and 673 cm⁻¹, corresponding to the $^{18}\text{O}^{16}\text{O}^{16}\text{O}$ and $^{18}\text{O}^{16}\text{O}^{18}\text{O}$ species, only appeared when the ice was warmed to 45 K. We note that a previous study in our groups suggested that the irradiated oxygen ices trap oxygen atoms at 11 K²⁷ such that, as the temperature increases, these oxygen atoms become mobile and can react with an oxygen atom or molecule to form molecular oxygen and ozone respectively. During the heating process additional bands of $^{16}\text{O}^{18}\text{O}^{16}\text{O}$ and $^{16}\text{O}^{16}\text{O}^{16}\text{O}$ appeared at 699 cm⁻¹ and 707 cm⁻¹, respectively. Finally, the weak ν_1 fundamental was observed at 1061 cm⁻¹ and 1090 cm⁻¹ (Fig. 1c); these absorptions correspond to the $^{18}\text{O}^{18}\text{O}^{16}\text{O}$ and $^{16}\text{O}^{16}\text{O}^{18}\text{O}$ isotopologues as evident from literature data.³⁰

3.2. Mass spectrometry

To monitor the subliming molecules, O_2 and O_3 containing both ^{16}O and ^{18}O were followed in real time by recording the ion currents of the mass-to-charge ratios (m/z) of 32 ($^{16}\text{O}_2^+$), 36 ($^{18}\text{O}_2^+$), 48 ($^{16}\text{O}_3^+$), 50 ($^{16}\text{O}_2^{18}\text{O}^+$), 52 ($^{18}\text{O}_2^{16}\text{O}^+$), and 54 ($^{16}\text{O}_3^+$). In the actual irradiation phase neither atomic oxygen, molecular oxygen, nor ozone were observed in the gas phase hence, since the detection limit of our mass spectrometer has been cited by the manufacturer to have partial pressures of about 1×10^{-15} torr, we conclude that no desorption occurs during irradiation. However dramatic changes were observed during the heating of the irradiated sample (Fig. 2). $^{32}\text{O}_2$ and $^{36}\text{O}_2$ were found to desorb when the temperature reaches 28 K and their yield is maximized at 35 K. All the ozone isotopomers and isotopologues were found to start to sublime from the ice at about 59 K. Simultaneous monitoring of the FTIR spectra and the ion currents in the gas phase reveals all ozone molecules had desorbed at 63 ± 1 K.

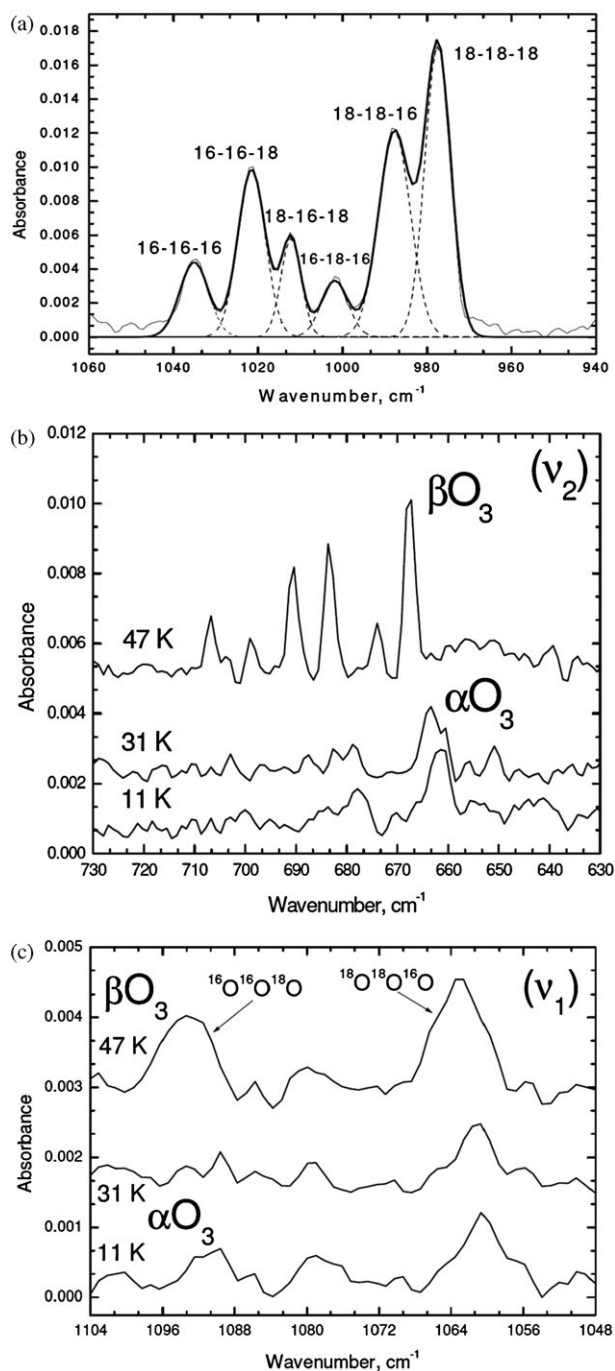


Fig. 1 (a) The deconvoluted ν₃ band of distinct O₃ isotopomers and isotopologues observed during irradiation at 11 K. (b) The ν₂ band of distinct O₃ isotopomers and isotopologues observed during the irradiation at 11 K and during warm-up at two different temperatures 31 and 47 K. (c) The ν₁ band of O₃ isotopomers and isotopologues observed during warm-up of the irradiated sample.

4. Discussion

4.1. Ozone formation during irradiation phase

Ozone was observed to form within the ices immediately after the electron irradiation commenced. Previous experiments on pure molecular oxygen ices (¹⁶O₂), which were irradiated under identical conditions as the isotopically mixed systems, suggested that upon

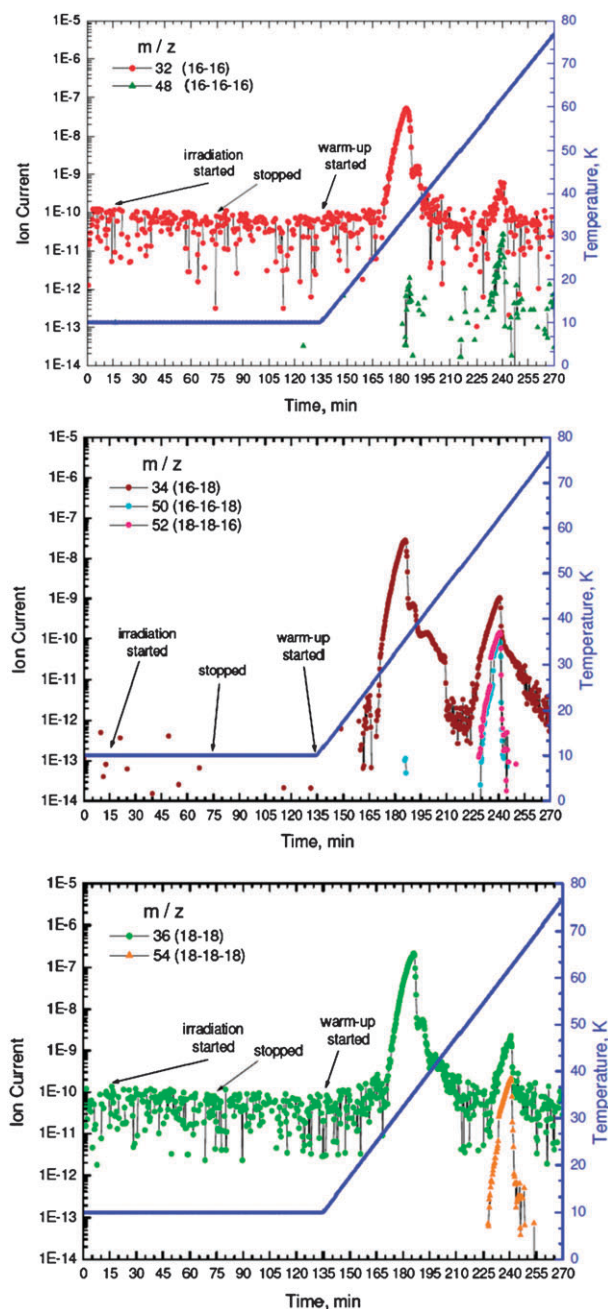
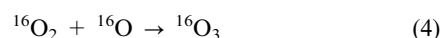
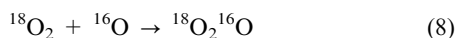
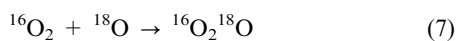
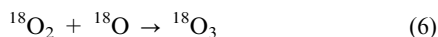


Fig. 2 Ion currents of subliming molecular oxygen (O₂) and ozone (O₃) isotopologues monitored *via* a quadrupole mass spectrometer during the warming up phase.

electron exposure, an oxygen molecule undergoes unimolecular decomposition to form two oxygen atoms (¹⁶O)²⁷ (reaction (3); term symbols are omitted for clarity). The released oxygen atom was found to react with a neighboring oxygen molecule to form an ozone molecule (¹⁶O₃) *via* eqn (4). Quantitatively, the temporal evolution of the ozone (¹⁶O₃) column density could be fit with (*pseudo*) first order kinetics.²⁷ Under these irradiation conditions, the back-dissociation of ozone to molecular oxygen and an oxygen atom was not found to play any significant role.²⁷





Analogous to these previous experiments, in a mixed isotope oxygen ice of $^{16}\text{O}_2$ and $^{18}\text{O}_2$, the production of ^{16}O and ^{18}O atoms *via* eqn (3) and (5) is expected. Here, the free ^{16}O and ^{18}O atoms can each react with $^{16}\text{O}_2$ and $^{18}\text{O}_2$ to form $^{16}\text{O}_3$ ($^{16}\text{O}_2/^{16}\text{O}$; eqn (4)), $^{18}\text{O}_3$ ($^{18}\text{O}_2/^{18}\text{O}$; eqn (6)), $^{16}\text{O}_2^{18}\text{O}$ ($^{16}\text{O}_2/^{18}\text{O}$; eqn (7)), and $^{18}\text{O}_2^{16}\text{O}$ ($^{18}\text{O}_2/^{16}\text{O}$; eqn (8)). It should be noted that $^{16}\text{O}_2^{18}\text{O}$ and $^{18}\text{O}_2^{16}\text{O}$ can be formed either in C_{2v} (symmetric) or C_s (asymmetric) structures, *i.e.* $^{16}\text{O}^{18}\text{O}^{16}\text{O}$ and $^{18}\text{O}^{16}\text{O}^{18}\text{O}$ as well as $^{16}\text{O}^{18}\text{O}^{18}\text{O}$ and $^{18}\text{O}^{16}\text{O}^{16}\text{O}$. Here, the reactive oxygen atom *formally* 'inserts' into the oxygen–oxygen bond giving the C_{2v} structures or can add to a terminal oxygen atom to form the C_s molecules. The temporal evolution of all these six ozone isotopomers and isotopologues are shown in Fig. 3 and are derived by plotting the column density of the deconvoluted ν_3 bands as depicted in Fig. 1a *versus* the time; the column densities are derived utilizing the corresponding integrated absorption coefficients as outlined in reference.²⁷ It should be noted that in order to obtain the relative abundances of these isotopomers and isotopologues it is important to correct each band area for the integrated absorption coefficient of the ν_3 band for that species. Unfortunately absorption coefficients for the different ozone isotopomers and isotopologues have not been measured so they were calculated utilizing the hybrid density functional B3LYP method^{32,33} with Dunning's aug-cc-pVTZ basis set³⁴ using the GAUSSIAN 98 quantum chemical program package.³⁵ It is important to note that computed, absolute absorption coefficients of individual vibrational normal modes may have uncertainties as large as 20%.^{36,37} Nevertheless if these coefficients are calculated using the same level of theory, the *relative* values of the absorption coefficients of different isotopically substituted ozone molecules will have much smaller uncertainties of only a few % and, since we are investigating the relative isotopic enrichment, this method is justified. Here, the integrated absorption coefficients for the ν_3 mode of the isotopomers and isotopologues have been computed to be 3.46×10^{-17} cm molecule⁻¹ (18–18–18), 3.32×10^{-17} cm molecule⁻¹ (18–18–16), 3.90×10^{-17} cm molecule⁻¹ (16–16–16), 3.54×10^{-17} cm molecule⁻¹ (16–16–18), 3.63×10^{-17} cm molecule⁻¹ (16–18–16), and 3.73×10^{-17} cm molecule⁻¹ (18–16–18).

A simple inspection of the column densities of the distinct isotopomers and isotopologues at the end of the irradiation exposure depicts surprising results. First, the 18–18–18 species formed *via* eqn (6) has column densities a factor of six higher than the corresponding 16–16–16 molecule (eqn (4)). On the other hand, the production of the C_{2v} symmetric 16–18–16 and 18–16–18 species are—within the error limits—identical. As a matter of fact these production rates are similar to the 16–16–16 isotopologues. Finally, the C_s species 18–18–16 are higher than the 16–16–18 molecule, but close to the column density of the 18–18–18 species. These data alone suggest that even in low temperature Solar System analog ices, energetic

electrons can induce significant isotope effects leading to a preferential formation of the heavier 18–18–18 *versus* 16–16–16 and a significantly enhanced formation of the heavy 18–18–16 *versus* 16–16–18. No isotopic effect was found in case of 16–18–16 *versus* 18–16–18.

In an attempt to understand the underlying reaction mechanisms, we fitted the column densities as compiled in Fig. 3 using two different kinetic models for ozone formation *via* (*pseudo*) first order kinetics (eqn (9); mechanism M1) or through a two-step mechanism (eqn (10); mechanism M2). M1 could characterize an end-on addition of the oxygen atom to the oxygen molecule; M2 might represent a consecutive reaction mechanism in which the oxygen atom first adds to the ring forming a cyclic ozone intermediate and then ring opens; alternatively, this two-step process could resemble the formation of free oxygen atoms forming first a $^{18}\text{O}^{16}\text{O}$ molecular oxygen species (step I) which then reacts with ^{18}O or ^{16}O to ozone (step II).

Again, as stated in the introduction, our experiments are designed to investigate if isotopic fractionation processes can occur in low temperature Solar System analog ices *via* non-equilibrium chemistry; therefore, the rate constants presented here refer to non-equilibrium rate constants, and cannot be compared with classical rate constants derived for isotopic enrichment studies in the gas phase. Eqn (9) and (10) mathematically describe a *pseudo* first order reaction $A \rightarrow B$ ⁸ and a consecutive two step process *via* the reaction sequence $A \rightarrow B \rightarrow C$ (eqn 10).²⁷ To present an unbiased and objective analysis, we fit the graphs of all isotopomers and isotopologues utilizing both models *via* M1 and M2. The rate constants of both fits are compiled in Tables 1 and 2, respectively.

$$[\text{O}_3](t) = a_1(1 - e^{-kt}) \quad (9)$$

$$[\text{O}_3](t) = (a_2/(k_2 - k_1))(k_2(1 - e^{-k_1t}) - k_1(1 - e^{-k_2t})) \quad (10)$$

The temporal evolutions can be fitted using eqn (9) (solid lines; Fig. 3; Table 1) utilizing rate constants between 2.7 and 4.2×10^{-2} s⁻¹. Eqn (10) also presented a reasonable fit of the measured column density profiles. Therefore, a kinematic analysis of the data suggests that the ozone isotopes can be formed either by a *pseudo* first order or second order reaction mechanism—or both. Both 16–18–16 and 18–16–18 could be formed *via* reaction of ^{18}O with $^{16}\text{O}_2$ and ^{16}O with $^{18}\text{O}_2$, respectively, *via* a cyclic ozone intermediate. Alternatively, an $^{16}\text{O}^{18}\text{O}$ molecule formed by recombination of ^{16}O and ^{18}O could react with ^{18}O or ^{16}O .

There has been a considerable debate as to the possibility in forming and stabilizing a ring structure of O_3 . It is estimated that the cyclic form of ozone lies ~ 1 eV above the dissociation limit.³⁸ Flemming *et al.*³⁹ have further argued that the lifetime of cyclic form at low temperatures may be greater than 30 seconds. We therefore searched for the evidence of this cyclic form which is predicted to have spectroscopic signatures to be at 1099.6 (ν_1), 782.9 (ν_2 , ν_3) cm⁻¹⁴⁰ (these values are for $^{48}\text{O}_3$), but we found no evidence for this form of ozone suggesting either that it is not formed or its lifetime is much shorter than Fleming *et al.* predict. The $^{16}\text{O}^{16}\text{O}^{16}\text{O}$ and $^{18}\text{O}^{18}\text{O}^{18}\text{O}$ isotopologues may be formed by either by the

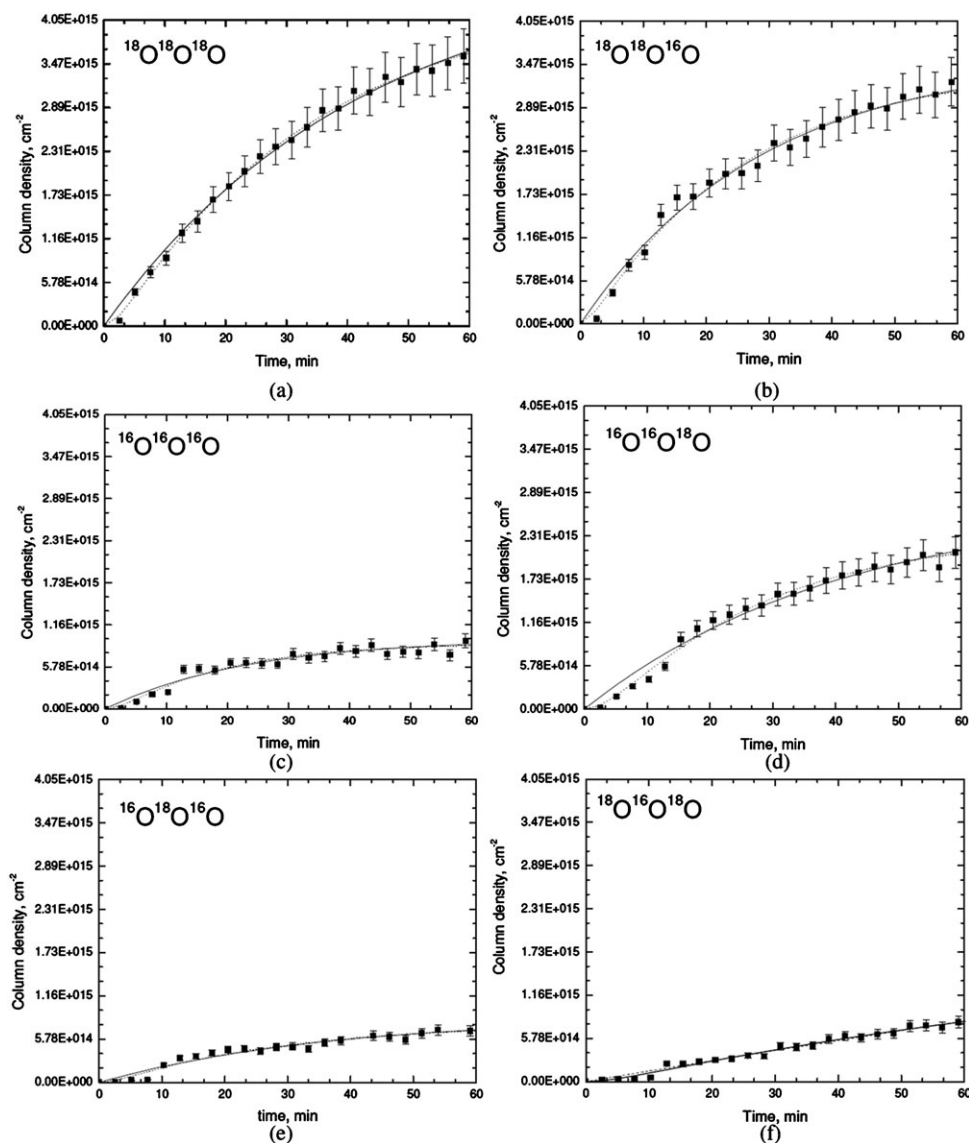


Fig. 3 Temporal evolution of ozone isotopomers and isotopologues in the ice during the irradiation at 10 K together with kinetic fits corresponding to *pseudo* first order reaction (given in eqn (3)) for (a) $^{18}\text{O}^{18}\text{O}^{18}\text{O}$, (b) $^{18}\text{O}^{18}\text{O}^{16}\text{O}$, (c) $^{16}\text{O}^{16}\text{O}^{16}\text{O}$, (d) $^{16}\text{O}^{16}\text{O}^{18}\text{O}$, (e) $^{16}\text{O}^{18}\text{O}^{16}\text{O}$, and a two step consecutive reaction for (f) $^{18}\text{O}^{16}\text{O}^{18}\text{O}$, given in eqn (4) respectively. Dotted lines show the fits using eqn (4) for a–d and using eqn (3) e–f.

Table 1 Rate coefficients obtained by fitting the temporal profiles of ozone isotopomers and isotopologues *via* eqn (9)

Reactants	Product	Rate coefficient (k/s^{-1})
$^{16}\text{O} + ^{16}\text{O}^{16}\text{O}$	$^{16}\text{O}^{16}\text{O}^{16}\text{O}$	$4.2 \pm 0.5 \times 10^{-2}$
$^{16}\text{O} + ^{18}\text{O}^{18}\text{O}$	$^{16}\text{O}^{18}\text{O}^{18}\text{O}$	$3.4 \pm 0.2 \times 10^{-2}$
$^{18}\text{O} + ^{18}\text{O}^{18}\text{O}$	$^{18}\text{O}^{18}\text{O}^{18}\text{O}$	$2.3 \pm 0.1 \times 10^{-2}$
$^{18}\text{O} + ^{16}\text{O}^{16}\text{O}$	$^{18}\text{O}^{16}\text{O}^{16}\text{O}$	$2.4 \pm 0.2 \times 10^{-2}$
$^{18}\text{O} + ^{16}\text{O}^{18}\text{O}$	$^{16}\text{O}^{18}\text{O}^{16}\text{O}$	$2.7 \pm 0.4 \times 10^{-2}$
$^{16}\text{O} + ^{18}\text{O}^{18}\text{O}$	$^{16}\text{O}^{18}\text{O}^{18}\text{O}$	$2.8 \pm 0.5 \times 10^{-2}$

end-on addition of ^{16}O to $^{16}\text{O}^{16}\text{O}/^{18}\text{O}$ to $^{18}\text{O}^{18}\text{O}$. Due to large concentrations of their parent molecules ($^{16}\text{O}^{16}\text{O}$ and $^{18}\text{O}^{18}\text{O}$) this is likely to be the dominant formation mechanism. It is also possible to conclude that the end-on addition to be the dominant pathway to produce $^{16}\text{O}^{16}\text{O}^{18}\text{O}$ and $^{18}\text{O}^{18}\text{O}^{16}\text{O}$ isotopologues, however we note that $^{16}\text{O}^{16}\text{O}^{16}\text{O}$ is produced with a quarter of the efficiency of the $^{18}\text{O}^{18}\text{O}^{18}\text{O}$ isotopologues.

Table 2 Rate coefficients obtained by fitting the temporal profiles of ozone isotopomers and isotopologues *via* eqn (10)

Product	Rate coefficients	
	k_1/s^{-1} (1st step)	k_2/s^{-1} (2nd step)
$^{16}\text{O}^{16}\text{O}^{16}\text{O}$	$5.6 \pm 1.3 \times 10^{-2}$	$4.0 \pm 3.2 \times 10^{-1}$
$^{18}\text{O}^{18}\text{O}^{18}\text{O}$	$2.9 \pm 0.1 \times 10^{-2}$	$4.9 \pm 0.9 \times 10^{-1}$
$^{18}\text{O}^{18}\text{O}^{16}\text{O}$	$3.9 \pm 0.5 \times 10^{-2}$	$7.5 \pm 6.1 \times 10^{-1}$
$^{16}\text{O}^{16}\text{O}^{18}\text{O}$	$3.9 \pm 0.5 \times 10^{-2}$	$2.3 \pm 0.7 \times 10^{-1}$
$^{18}\text{O}^{16}\text{O}^{18}\text{O}$	$0.9 \pm 0.5 \times 10^{-2}$	$2.7 \pm 1.5 \times 10^{-1}$
$^{16}\text{O}^{18}\text{O}^{16}\text{O}$	$3.5 \pm 0.8 \times 10^{-2}$	$4.7 \pm 4.3 \times 10^{-1}$

4.2. Ozone formation during warm-up

After irradiation the sample was kept under isothermal conditions for an hour before the irradiated ice was warmed at the rate of 0.5 K min^{-1} . After the irradiation oxygen atoms are still trapped in the ice matrix.²⁷ Although $\text{O}(\text{D})$ can be

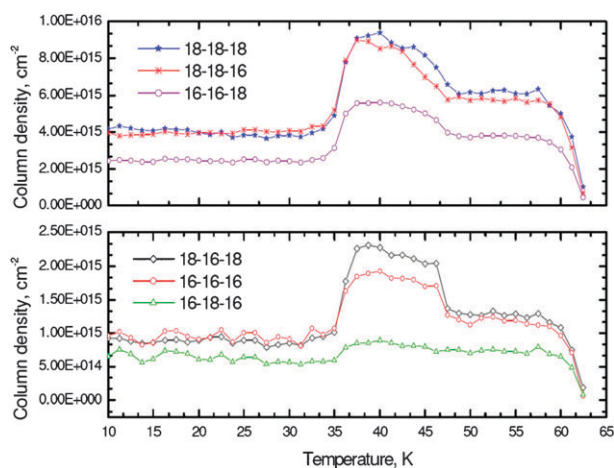


Fig. 4 ν_3 Band area of ozone isotopomers and isotopologues during warm-up of the sample at the rate of 0.5 K min^{-1} for the sample irradiated at $\sim 11 \text{ K}$. Error bars not shown for clarity.

produced in the matrix during irradiation, after 3600 s in the isothermal condition all these atoms will have relaxed into their ground state leaving the irradiated ice rich in atomic oxygen in its ground state (^3P).²⁷ As the temperature is increased, these oxygen atoms start to diffuse forming (i) molecular oxygen due to recombination of oxygen atoms and (ii) ozone due to the addition of oxygen atoms to the nascent molecular oxygen.²⁷ This explains our observation of an increased ozone production during temperature programmed desorption for all six ozone isotopomers and isotopologues (Fig. 4). After the oxygen molecules have desorbed from the surface at around 35 K, no further increase in ozone production is observed and only ozone is left on the surface. However at about 47 K, novel bands appear in the infrared spectra indicating a change of phase from the α (amorphous) to β (crystalline) ozone (Fig. 1(b and c)). All ozone isotopomers and isotopologues have sublimed from the surface at around 63 K.

5. Conclusion

We have studied the formation of six ozone isotopomers and isotopologues in electron-irradiated solid oxygen $^{16}\text{O}_2$ and $^{18}\text{O}_2$ (1 : 1) at 11 K. These are: $^{16}\text{O}^{16}\text{O}^{16}\text{O}$, $^{18}\text{O}^{18}\text{O}^{18}\text{O}$, $^{16}\text{O}^{16}\text{O}^{18}\text{O}$, $^{18}\text{O}^{18}\text{O}^{16}\text{O}$, $^{16}\text{O}^{18}\text{O}^{16}\text{O}$, and $^{18}\text{O}^{16}\text{O}^{18}\text{O}$. We have shown that under such conditions there are profound isotope effects which are induced by non-equilibrium chemistry. The heavy $^{18}\text{O}^{18}\text{O}^{18}\text{O}$ species is formed with factor of about six more than the corresponding $^{16}\text{O}^{16}\text{O}^{16}\text{O}$ molecule. Likewise, the heavy $^{18}\text{O}^{18}\text{O}^{16}\text{O}$ species is formed with abundances of about a factor of three higher than the lighter $^{16}\text{O}^{16}\text{O}^{18}\text{O}$ counterpart. No isotope effect was observed in the production of $^{16}\text{O}^{18}\text{O}^{16}\text{O}$ versus $^{18}\text{O}^{16}\text{O}^{18}\text{O}$. The production of distinct ozone isotopomers and isotopologues by irradiation of oxygen ices with high energy electrons is relevant in the magnetosphere of the giant planets Jupiter and Saturn, where similar mechanisms may lead to the ^{18}O enrichment on the icy satellites of Jupiter and Saturn. Whether such ^{18}O enrichment occurs in more complex ices (e.g. carbon dioxide, water, and oxygen rich ices more typical of planetary surfaces) remains to

be seen in future laboratory experiments. Likewise, although we have presented solid evidence for the fact that energetic electrons can lead to a ^{18}O enrichment in ozone in irradiated oxygen ices, the underlying reaction mechanisms and possible involvement of 'cyclic ozone' still remains to be resolved. Does a symmetry-induced isotopic fractionation present a valid answer even in low temperature Solar System ices?^{17,19,20} Or can a symmetry-based dynamical effect, as suggested for calcium-aluminium rich inclusions in meteorites, be the source of these enrichment processes?⁴¹ Likewise, these processes could also involve long-lived resonances in the delta zero-point energies.⁴² For completeness, we should also state that we have no evidence for radiation induced tetraoxygen molecules (O_4). These issues remain to be investigated theoretically in the future.

Acknowledgements

One of us (BS) acknowledges receipt of a Postgraduate studentship from the Open University. RIK thanks the National Aeronautics Space Administration (NASA Astrobiology Institute under Cooperative Agreement no. NNA09DA77A issued through the Office of Space Science) for funding.

References

- 1 R. N. Clayton, Oxygen Isotopes in Meteorites, *Annu. Rev. Earth Planet. Sci.*, 1993, **21**, 115–149.
- 2 R. N. Clayton, T. K. Mayeda, J. N. Goswami and E. J. Olsen, Oxygen Isotope Studies of Ordinary Chondrites, *Geochim. Cosmochim. Acta*, 1991, **55**, 2317–2337.
- 3 I. P. J. Taylor, M. B. Duke, L. T. Silver and S. Epstein, Oxygen isotope studies of minerals in stony meteorites, *Geochim. Cosmochim. Acta*, 1965, **29**, 489–512.
- 4 M. Ozima, F. A. Podosek, T. Higuchi, Q.-Z. Yin and A. Yamada, On the mean oxygen isotope composition of the Solar System, *Icarus*, 2007, **186**, 562–570.
- 5 D. S. Burnett, The Genesis Discovery Mission: Return of Solar Matter to Earth, *Space Sci. Rev.*, 2003, **105**, 509–534.
- 6 K. D. McKeegan, J. Aleon, J. Bradley, D. Brownlee, H. Busemann, A. Butterworth, M. Chaussidon, S. Fallon, C. Floss, J. Gilmour, M. Gounelle, G. Graham, Y. Guan, P. R. Heck, P. Hoppe, I. D. Hutcheon, J. Huth, H. Ishii, M. Ito, S. B. Jacobsen, A. Kearsley, L. A. Leshin, M.-C. Liu, I. Lyon, K. Marhas, B. Marty, G. Matrajt, A. Meibom, S. Messenger, S. Mostefaoui, S. Mukhopadhyay, K. Nakamura-Messenger, L. Nittler, R. Palma, R. O. Pepin, D. A. Papanastassiou, F. Robert, D. Schlutter, C. J. Snead, F. J. Stadermann, R. Stroud, P. Tsou, A. Westphal, E. D. Young, K. Ziegler, L. Zimmermann and E. Zinner, Isotopic Compositions of Cometary Matter Returned by Stardust, *Science*, 2006, **314**, 1724–1728.
- 7 M. J. Spicuzza, J. M. D. Day, L. A. Taylor and J. W. Valley, Oxygen isotope constraints on the origin and differentiation of the Moon, *Earth Planet. Sci. Lett.*, 2007, **253**, 254–265.
- 8 B. Larsson, Molecular oxygen in the ρ Ophiuchi cloud, *Astron. Astrophys.*, 2007, **466**, 999–1003.
- 9 M. H. Thiemens, Atmospheric Science: The Mass-Independent Ozone Isotope Effect, *Science*, 2001, **293**, 226.
- 10 M. H. Thiemens and T. Jackson, Pressure dependency for heavy isotope enhancement in ozone formation, *Geophys. Res. Lett.*, 1990, **17**, 717–719.
- 11 M. H. Thiemens and T. Jackson, New experimental evidence for the mechanism for production of isotopically heavy O_3 , *Geophys. Res. Lett.*, 1988, **15**, 639–642.
- 12 J. Morton, J. Barnes, B. Schueler and K. Mauersberger, Laboratory studies of heavy ozone, *J. Geophys. Res.*, 1990, **95**, 901–907.

- 13 J. E. Heidenreich III and M. H. Thieme, A non-mass-dependent isotope effect in the production of ozone from molecular oxygen, *J. Chem. Phys.*, 1983, **78**, 892–895.
- 14 K. Mauersberger, Ozone isotope measurements in the stratosphere, *Geophys. Res. Lett.*, 1987, **14**, 80–83.
- 15 D. Krankowsky, P. Lammerz and K. Mauersberger, Isotopic measurements of stratospheric ozone, *Geophys. Res. Lett.*, 2000, **27**, 2593–2596.
- 16 A. A. Penzias, The Isotopic Abundances of Inter-Stellar Oxygen, *Astrophys. J.*, 1981, **249**, 518–523.
- 17 G. I. Gellene, An Explanation for Symmetry-Induced Isotopic Fractionation in Ozone, *Science*, 1996, **274**, 1344–1346.
- 18 K. Mauersberger, B. Erbacher, D. Krankowsky, J. Guuml;ntner and R. Nickel, Ozone Isotope Enrichment: Isotopomer-Specific Rate Coefficients, *Science*, 1999, **283**, 370–372.
- 19 C. Janssen and R. A. Marcus, Does Symmetry Drive Isotopic Anomalies in Ozone Isotopomer Formation?, *Science*, 2001, **294**, 951a.
- 20 Y. Q. Gao and R. A. Marcus, Strange and Unconventional Isotope Effects in Ozone Formation, *Science*, 2001, **293**, 259–263; Y. G. Gao and R. A. Marcus, An approximate theory of the ozone isotopic effects: rate constant ratios and pressure dependence, *J. Chem. Phys.*, 2007, **127**, 244316.
- 21 N. W. Larsen, T. Pedersen and J. Sehested, Isotopic Study of the Mechanism of Ozone Formation, *Int. J. Chem. Kinet.*, 1991, **23**, 331–343.
- 22 C. Janssen, J. Guenther, D. Krankowsky and K. Mauersberger, Relative formation rates of O-50(3) and O-52(3) in O-16–O-18 mixtures, *J. Chem. Phys.*, 1999, **111**, 7179–7182.
- 23 V. A. Krasnopolsky, J. P. Maillard, T. C. Owen, R. A. Toth and M. D. Smith, Oxygen and carbon isotope ratios in the martian atmosphere, *Icarus*, 2007, **192**, 396–403.
- 24 K. S. Noll, R. E. Johnson, A. L. Lane, D. L. Domingue and H. A. Weaver, Detection of ozone on Ganymede, *Science*, 1996, **273**, 341–343.
- 25 K. S. Noll, T. L. Roush, D. P. Cruikshank, R. E. Johnson and Y. J. Pendleton, Detection of ozone on Saturn's satellites Rhea and Dione, *Nature*, 1997, **388**, 45–47.
- 26 B. D. Teolis, M. J. Loeffler, U. Raut, M. Fama and R. A. Baragiola, Ozone synthesis on the icy satellites, *Astrophys. J.*, 2006, **644**, L141–L144.
- 27 C. J. Bennett and R. I. Kaiser, Laboratory studies on the formation of ozone (O-3), on icy satellites and on interstellar and cometary ices, *Astrophys. J.*, 2005, **635**, 1362–1369.
- 28 L. Andrews and R. C. J. Spiker, Argon matrix Raman and infrared spectra and vibrational analysis of ozone and the oxygen-18 substituted ozone molecules, *J. Phys. Chem.*, 1972, **76**, 3208–3213.
- 29 L. Schrivermazzuoli, A. Desaxce, C. Lugez, C. Camypeyret and A. Schriver, Ozone Generation through Photolysis of an Oxygen Matrix at 11-K-Fourier-Transform Infrared-Spectroscopy Identification of the O-18-O-3 Complex and Isotopic Studies, *J. Chem. Phys.*, 1995, **102**, 690–701.
- 30 L. Schrivermazzuoli, A. Schriver, C. Lugez, A. Perrin, C. CamyPeyret and J. M. Flaud, Vibrational spectra of the O-16/O-17/O-18 substituted ozone molecule isolated in matrices, *J. Mol. Spectrosc.*, 1996, **176**, 85–94.
- 31 M. Spoliti, S. N. Cesaro and B. Mariti, Infrared-Spectrum and Geometry of Ozone Isolated in Inert-Gas Matrices at 20.4 K, *J. Chem. Phys.*, 1973, **59**, 985–986.
- 32 A. D. Becke, Density-functional thermochemistry. III. The role of exact exchange, *J. Chem. Phys.*, 1993, **98**, 5648–5652.
- 33 C. Lee, W. Yang and R. G. Parr, Development of the Colle–Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B: Condens. Matter*, 1988, **37**, 785–789.
- 34 T. H. Dunning, Jr., Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen, *J. Chem. Phys.*, 1989, **90**, 1007–1023.
- 35 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, *Gaussian 98, Revision A.9*, Gaussian, Inc., Pittsburgh PA, 1998.
- 36 C. J. Cramer, *Essentials of Computational Chemistry*, Wiley, Chichester, England, 2002, p. 306.
- 37 B. Galabov, T. Dudev, S. Ilieva and J. R. Durig, Creation of intensity theory in vibrational spectroscopy: Key role of *ab initio* quantum mechanical calculations, *Int. J. Quantum Chem.*, 1998, **70**, 331–339.
- 38 L. DeVico, L. Pegado, J. Heimdal, P. Soederhjelm and Bjoern O. Roos, The ozone ring closure as a test for multi-state multi-configurational second order perturbation theory (MS-CASPT2), *Chem. Phys. Lett.*, 2008, **461**, 136.
- 39 B. Flemmig, P. T. Wolczanski and R. Hoffmann, Transition Metal Complexes of Cyclic and Open Ozone and Thiozone, *J. Am. Chem. Soc.*, 2005, **127**, 1278–1285.
- 40 R. Elliott, R. Compton, R. Levis and S. Matsika, Excited Electronic States of the Cyclic Isomers of O₃ and SO₂, *J. Phys. Chem. A*, 2005, **109**, 11304–11311.
- 41 R. A. Marcus, Mass-independent isotopic effect in the earliest processed solids in the solar system: A possible mechanism, *J. Chem. Phys.*, 2004, **121**, 8201.
- 42 E. Vetoshkin and D. Babikov, Semiclassical wave packet study of anomalous isotope effect in ozone formation, *J. Chem. Phys.*, 2007, **127**, 154312.